Matrix-Isolation of Iodine Superoxide and Iodine Dioxide

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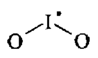
Flash pyrolysis of a gas mixture containing iodine, oxygen and argon yields the hitherto unknown iodine superoxide, which can be identified by its UV absorption (λ_{max} = 254 nm) after trapping the pyrolysate at 12 K. Irradiation converts iodine superoxide into iodine dioxide, identified by its IR and UV spectra.

In 1844 Millon prepared the first iodine oxide[1], later identified by Kappeler as diiodine tetroxide I_2O_4 (**1**)[2]. However, even today our knowledge of the oxides of iodine is rather fragmentary. The well-characterized compounds I_2O_4 (**1**)[3], I_2O_5 (**2**)[4] and I_2O_6 (**3**)[5] all have polymeric structures and decompose on heating. Little is known about the identity and structure of the solid I_4O_9 (**4**)[6].

$(I_2O_4)_n$ **1** $(I_2O_5)_n$ **2** $(I_2O_6)_n$ **3** $(I_4O_9)_n$ **4**

$IO^\bullet$

5



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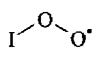

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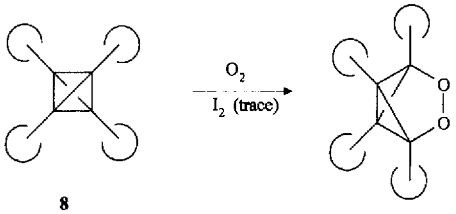
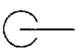
In contrast to the chlorine compounds only one iodine oxide with monomeric structure, the radical monoxide $IO^\bullet$ (**5**), has been characterized beyond doubt[7]. For monomeric iodine dioxide $OIO^\bullet$ (**6**) solely the ESR spectrum was reported[8]. The appearance of **6** as an intermediate in the flash photolysis and pulse radiolysis of aqueous iodate solutions has been the subject of some debate[9]. Buxton and Sellers finally showed that a UV absorption at 490 nm, originally attributed to the neutral radical $OIO^\bullet$ (**6**), is due to the species IO_3^{2-} instead[10].

Our motivation for an examination of the system I_2/O_2 had two different origins. Firstly, the flash pyrolysis of gas mixtures $Br_2/O_2/Ar$ and subsequent photolysis of the pyrolysate turned out to be a new and convenient route for the matrix-isolation of the two isomers bromine superoxide $BrOO^\bullet$ and bromine dioxide $OBrO^\bullet$[11]. The question arose as to whether the flash pyrolysis of a gas mixture $I_2/O_2/Ar$ would lead analogously to the formation of the hitherto unknown iodine superoxide $IOO^\bullet$ (**7**) and upon photolysis to iodine dioxide $OIO^\bullet$ (**6**).

Secondly, in the course of our studies on tetra-*tert*-butyltetrahedrane (**8**) we found a unique oxidation reaction. A cyclic peroxide (**9**) was the only product, when **8** was treated with oxygen in presence of traces of iodine[12]. We had reasons to assume, that in this reaction the attacking oxygen was activated by the iodine – perhaps by the formation of a complex between oxygen and iodine – rather than the substrate **8** via a SET process. This type of oxygen activation with iodine had not to our knowledge been reported in the literature. Thus a better understanding of the system I_2/O_2 was desirable.



8 **9**

 ≙ $(CH_3)_3C$-

Matrix-Isolation Experiments

A gas mixture $I_2/O_2/Ar$ was subjected to a high-vacuum flash pyrolysis at 900°C and the pyrolysate was trapped on a cold CsI window (12 K). The UV spectrum is shown in Figure 1 and exhibits, apart from the absorption of iodine[13], a new UV band with λ_{max} = 254 nm. Considering the known UV absorptions of $ClOO^\bullet$ (λ_{max} = 247 nm)[14] and $BrOO^\bullet$ (λ_{max} = 262 nm)[11] we assign this UV band to iodine superoxide $IOO^\bullet$ (**7**). In accordance with the observation that the UV absorption of $BrOO^\bullet$ is much stronger than its IR band, it is not too surprising that no corresponding IR spectrum of **7** could be detected.

This reflects the decreasing stability of halogen superoxides with increasing atomic number of the halogen: While chlorine superoxide $ClOO^\bullet$ can even be observed in the gas phase[14], the identification of $BrOO^\bullet$ by its IR and UV spectra was only possible under matrix conditions[11]. In the case of $IOO^\bullet$ (**7**) the concentration of generated and matrix-isolated molecules is too low to obtain a measurable IR absorption.

Figure 1. UV spectrum of IOO• (7)

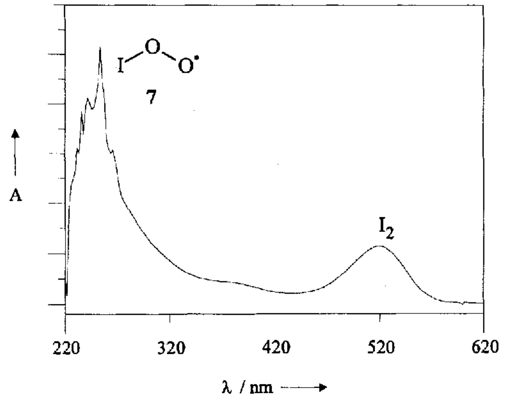


Figure 2. UV spectrum of OIO• (6). The numbers assign the corresponding progression

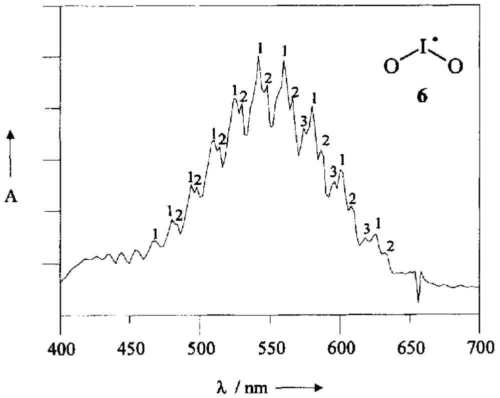


Table 1. UV absorptions (nm) of OIO• (**6**)

Series 1	Series 2	Series 3
467		
480	483	
494	498	
509	514	
525	530	
542	548	
560	566	574
580	587	596
601	609	618
626	634	

Obviously the tendency to decompose to X• and O_2 increases with increasing mass of the halogen X•. These findings can be rationalized by the decreasing X-OO bond energy: In contrast to the values for FOO• (≈ 49 kJ/mol)[15a] and ClOO• (≈ 20 kJ/mol)[15b] no experimental data for BrOO• are known. An estimated bond dissociation energy of 3.9 kJ/mol was based on a radical-molecule complex[15c] and seems to be too low, considering the experimental observation of BrOO•[11]. However, the dissociation energy of the bromine compound is expected to be considerably smaller than the known value for the chlorine compound[15d]. Thus, the low stability of BrOO• is apparent. It can be assumed from these figures, that the bond energy of **7** is even lower than the corresponding value of BrOO•. In this context, the question arises whether **7** should really be described as a molecule with a distinct covalent iodine-oxygen bond or should better be described as a complex between the iodine atom and the oxygen molecule.

Upon short irradiation (20 min) with 254 nm light, the UV band of **7** vanished and a new UV absorption of iodine dioxide OIO• (**6**) with a maximum at about 550 nm appeared. The structured band of **6** shows a progression of strong doublets (lower wavelengths: series 1; higher wavelengths: series 2) and a very weak third progression (series 3). Band positions of all three series are given in Table 1. The spectrum is shown in Figure 2, in which the series are marked with the corresponding numbers.

In view of the fact that the UV spectrum of OIO• (**6**) is very similar to the UV spectra of OClO• (λ_{max} ≈ 360 nm)[14] and OBrO• (λ_{max} ≈ 490 nm)[11,16] we interpret the structured band of **6** in analogy to an assignment made earlier for OBrO•[16]. According to this assignment the progressions are caused by the vibrational structure within the electronic transition $A^2A_2 \leftarrow X^2B_1$. Series 2 can be attributed to the excitation of the symmetric stretching vibration $(v_n, 0, 0) \leftarrow (0, 0, 0)$, while series 1 results from a combination of bending and symmetric stretching vibrations $(v_n, 1, 0) \leftarrow (0, 0, 0)$. The very weak third progression involves two quanta of the bending vibration together with the symmetric stretching vibration $(v_n, 2, 0) \leftarrow (0, 0, 0)$.

In the IR spectrum, in addition to the ozone bands at 1038.5 and 1033.2 cm^{-1}, two new bands appeared simultaneously with the UV absorptions at 550 nm and hence were also assigned to **6**. The asymmetric stretching vibration v_3 (800.3 cm^{-1}) and the symmetric stretching vibration v_1 (768.0 cm^{-1}) could be observed (see Table 2 and Figure 3).

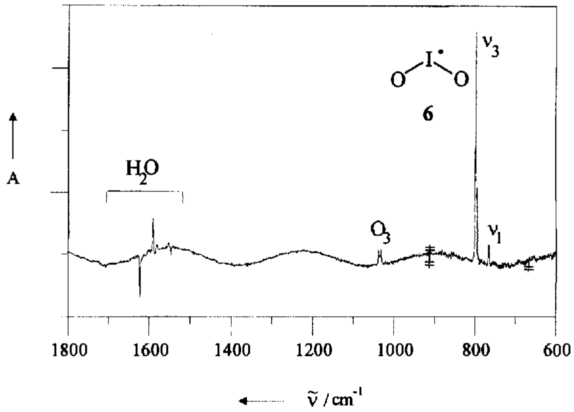
Table 2. IR absorptions [cm^{-1}] and rel. intensities (exp.: peak areas) of OIO• (**6**)

O_2/Ar matrix	O_2 matrix	Assignment
800.3 (1.00)	801.3 (1.00)	v_3 (OIO)[b]
798.9[a]	796.5[a]	
797.4[a]		
795.4[a]		
768.0 (0.11)	769.5 (0.12)	v_1 (OIO)[c]
766.1[a]	768.0[a]	

[a] Band split due to site effects. – [b] Asymmetric stretching vibration. – [c] Symmetric stretching vibration.

The band positions in the IR spectrum give strong indications of the bonding character in OIO• (**6**). In the IR and Raman spectra of I_2O_4 (**1**)[17a], I_2O_5 (**2**)[17a] and I_4O_9 (**4**)[6] bands at about 800 cm^{-1} were found, which, in accordance with the corresponding crystal structures, can be attributed to an I=O "double bond" stretching vibration (on the basis of the observed absorptions a force constant of 5.15 mdyn/Å was deduced[17b], which gives, using Sieberts rule, a bond order of 1.51[17c]). For I–O "single" bonds, on the other hand, IR absorptions at about 600 cm^{-1} were observed. On the basis of these figures, one can argue that the IO bond in OIO• (**6**) possesses some double-bond character. This may be explained by π-back-bonding from a filled p-orbital

Figure 3. IR spectrum of OIO$^•$ (**6**). The experimental spectrum is a difference spectrum of the matrix-isolated pyrolysate after irradiation of IOO$^•$ (**7**) with 254 nm light (positive values) and before irradiation (negative values)



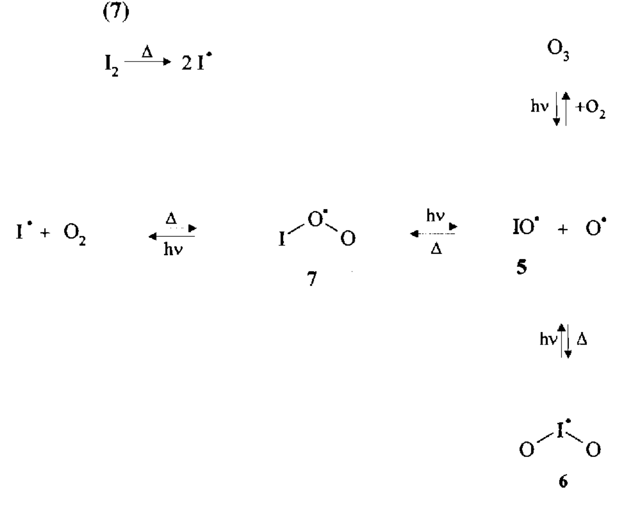
on the oxygen atoms to an empty d- (or f-) orbital of iodine in addition to the regular σ-bond.

Irradiation with wavelengths longer than 395 nm caused a decrease in the amount of **6** and a reversion to **7** (as indicated by the UV spectra). This interconversion is an additional structural proof for both isomers **6** and **7**.

Flash pyrolysis of a gas mixture of I_2 and O_2 only (no argon added), followed by the photolysis of the matrix-isolated pyrolysate with 254 nm light, also led to the formation of OIO$^•$ (**6**). Due to the poor transparency of the oxygen matrix no UV spectrum could be recorded.

If the pyrolysate of a gas mixture $I_2/O_2/Ar$ was exposed to a long-term irradiation (17 h) with 254 nm light, in addition to the UV band of **6** the UV progression band of iodine monoxide IO$^•$ (**5**) at $\lambda_{max} \approx 430$ nm appeared[18]. We thus assume that the photochemical isomerization between iodine superoxide IOO$^•$ (**7**) and iodine dioxide OIO$^•$ (**6**) proceeds via **5** as an intermediate. The oxygen atoms formed in this reaction can be trapped by oxygen molecules with the formation of ozone.

Scheme 1. Generation and photochemical isomerization of IOO$^•$ (**7**)



Scheme 1, which is similar to that used for the Br_2/O_2 system (for a detailed discussion see Ref.[11]), summarizes the observations and shows that iodine and bromine are very similar in their behaviour towards oxygen.

Conclusion

Thermally generated iodine atoms react with molecular oxygen to produce iodine superoxide IOO$^•$ (**7**). This species might be the reactive intermediate responsible for a catalytic activation of oxygen by iodine. Upon photolysis **7** isomerizes into iodine dioxide OIO$^•$ (**6**).

Experimental Section

Equipment for matrix isolation, photolysis, and pyrolysis: Ref.[19].

Commercially available iodine (Merck, doubly sublimed), oxygen (Messer Griesheim, 4.5) and argon (Messer Griesheim, 4.8) were used without further purification.

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[1] M. E. Millon, *Ann. Chim. et Phys.* **1844**, *12*, 345–352, 353–360.

[2] H. Kappeler, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 3496–3501.

[3] H. Fjellvåg, A. Kjekshus, *Acta Chem. Scand.* **1994**, *48*, 815–822.

[4] K. Selte, A. Kjekshus, *Acta Chem. Scand.* **1970**, *24*, 1912–1924.

[5] T. Kraft, M. Jansen, *J. Am. Chem. Soc.* **1995**, *117*, 6795–6796.

[6] S. Sunder, J. C. Wren, A. C. Vikis, *J. Raman Spectrosc.* **1985**, *16*, 424–426.

[7] R. A. Cox, G. B. Coker, *J. Phys. Chem.* **1983**, *87*, 4478–4484 and refs. cited therein.

[8] N. M. Atherton, J. R. Morton, K. F. Preston, S. J. Strach, *J. Chem. Phys.* **1981**, *74*, 5521–5525; J. R. Byberg, *J. Chem. Phys.* **1986**, *85*, 4790–4793.

[9] [9a] O. Amichai, A. Treinin, *J. Phys. Chem.* **1970**, *74*, 830–835. – [9b] F. Barat, L. Gilles, B. Hickel, J. Sutton, *J. Chem. Soc., Chem. Commun.* **1969**, 1485. – [9c] O. Amichai, A. Treinin, *J. Chem. Phys.* **1970**, *53*, 444–445. – [9d] F. Barat, L. Gilles, B. Hickel, B. Lesigne, *J. Phys. Chem.* **1972**, *76*, 302–307. – [9e] Y. Tendler, M. Faragi, *J. Chem. Phys.* **1973**, *58*, 848–853. – [9f] I. Wagner, H. Strehlow, *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 297–301.

[10] G. V. Buxton, R. M. Sellers, *J. Chem. Soc., Faraday Trans. 1*, **1985**, *81*, 449–471.

[11] G. Maier, A. Bothur, *Z. Anorg. Allg. Chem.* **1995**, *621*, 743–746.

[12] G. Maier, *Angew. Chem.* **1988**, *100*, 317–341; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309–332.

[13] L. Andrews, *J. Am. Chem. Soc.* **1976**, *98*, 2152–2156.

[14] H. S. P. Müller, H. Willner, *J. Phys. Chem.* **1993**, *97*, 10589–10598.

[15] [15a] P. Pagsberg, E. Ratajcak, A. Sillesen, J. T. Jodkowski, *Chem. Phys. Lett.* **1987**, *141*, 88–94. – [15b] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, J. Troe, *J. Chem. Phys.* **1991**, *95*, 6463–6470. – [15c] J. A. Blake, R. J. Browne, G. Burns, *J. Chem. Phys.* **1970**, *53*, 3320–3323. – [15d] *Gmelin's* Handbook of Inorganic and Organometallic Chemistry, Bromine, Supplement Vol. B2, 8. Edit., Springer-Verlag, Berlin, **1992**.

[16] O. V. Rattigan, R. L. Jones, R. A. Cox, *Chem. Phys. Lett.* **1994**, *230*, 121–126.

[17] [17a] O. H. Ellestad, T. Woldbæk, A. Kjekshus, P. Klæboe, K. Selte, *Acta Chem. Scand. Ser. A*, **1981**, *35*, 155–164. – [17b] N. B. Colthup, L. H. Daly, S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 2nd ed., Academic Press, New York, **1975**. – [17c] A. Fadini, *Molekülkraftkonstanten*, Steinkopff Verlag, Darmstadt, **1976**.

[18] A. Loewenschuss, J. C. Miller, L. Andrews, *J. Mol. Spectrosc.* **1980**, *81*, 351–362.

[19] G. Maier, J. Eckwert, A. Bothur, H. P. Reisenauer, C. Schmidt, *Liebigs Ann.* **1996**, *7*, 1041–1053.

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